Substructures of Colloidal Silver Particles (Commemoration Issue Dedicated to Professor Rempei Gotoh On the Occasion of his Retirement)

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Finely dispersed particles of silver sols prepared by the photochemical reduction of silver solutions in the presence of sodium dodecyl sulfate were examined by high resolution electron microscopy. Most of the particles whose size ranged from 100 to 1000 A exhibited characteristic diffraction contrasts which were analysed to reveal that the fine particles, identified as metallic silver by electron diffraction, included disorders such as stacking faults, crossed faults, twins all associated with {111} planes of f.c.c. lattice. Multiple twin configuration which consisted of five {111} tetrahedra to form decahedron as a whole was frequently observed for the first time as the example of metallic particles grown from aqueous solutions.

INTRODUCTION

Although it is a well known fact nowadays that a metallic sol contains small particles as one of its major constituents, no much attention had been paid to the morphological aspects other than their size distribution until the electron microscope was first accepted as a promising instrument for the observation of an object smaller than the wave length of the ordinary light. In fact, it was almost three decades ago when Borries and Kausche[1] examined gold sol particles with their incipient electron microscope to indicate that the individual particles appeared as polyhedra the size of which ranged 5 to 50 mμ in diameter. They actually deduced on the basis of geometric analysis that the polygonal particles they observed were mostly cubes and cube-octahedra which produced various silhouettes such as squares, hexagons, octagons and dodecagons depending upon the different orientation of each particle with respect to the fixed direction, that is, the optical axis of the electron microscope. Since metallic gold assumes a face-centered cubic lattice, such a deduction may be reasonably acceptable provided that the individual particles were nothing but a single crystal as implicitly required as a basic assumption.

In order for the crystal structure of each particle to be determined, the electron diffraction should have been well applicable. However, it was only for particular gold sol particles[2] with thin plate-like crystal habit that the selected area electron diffraction was effectively applied as the combined use with the microscopy for the determination of the lattice orientation as well as the crystal structure. Recently, the resolving power of an electron microscope has been extraordinarily improved so that metallic particles even less than 10 A in diame-

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ter can be clearly recognized. As the efficiency of the instrument and the technique of specimen preparation were greatly improved, the theoretical bases[3] on which the interpretation of a recorded image was brought about have also been fruitfully developed for the last decade, particularly in regard to the relationship[4] between the various contrasts and the microstructures such as lattice defects, twins, superlattice and so forth.

By the application of high resolution electron microscopy, we tried to find out how the smallest existing particle could assume a definite crystal structure and crystal habit with regard to various metallic sols such as colloidal gold and colloidal silver. The results were rather surprising in a sense that most of the dispersed particles were not single crystals but composed of smaller crystallites although their combination appeared in certain regularities instead of being in random polycrystalline states. This paper is to report the results of the morphological analysis with regard to colloidal silver particles. It seems also advisable to emphasize the significance of the appearance of such sol particles with regular combination of crystallites if one tries to understand the real mechanism of the nucleation and growth of colloidal particles from solutions.

SAMPLES AND ANALYTICAL PROCEDURE

The silver sols used in the present work were prepared by the photochemical reduction of aqueous solutions of silver nitrate mixed with sodium dodecyl sulfate which was added as the protective colloid. The color of the resulted sols changed from yellowish brown to reddish brown depending upon the preparing condition. Though the procedure and the mechanism of photochemical formation of silver sol in the presence of SDS seem to be worthnoting, they will not be discussed here in detail.

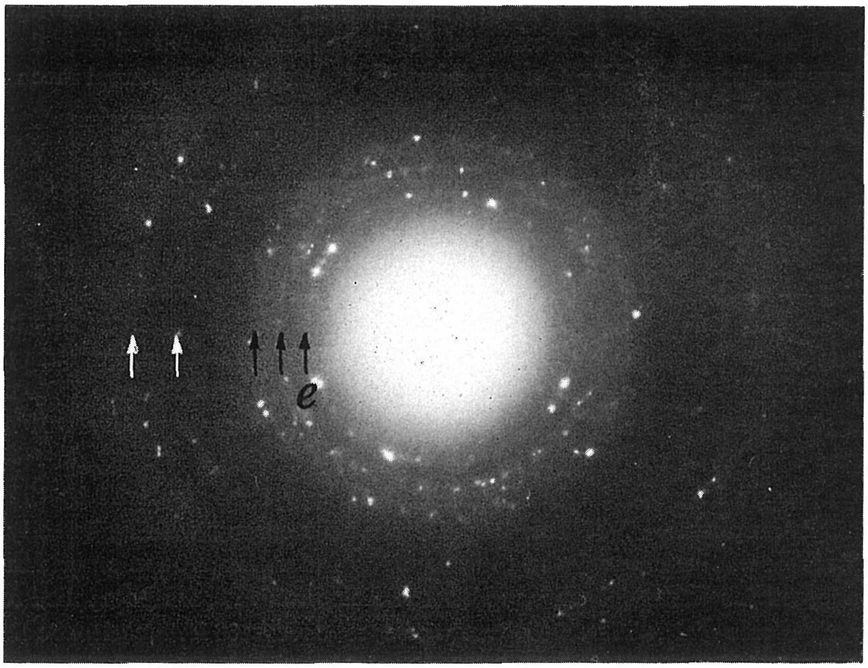
The practical specimens for electron microscopy were prepared by the ordinary single-drop method. Since the electron microscopy with sufficiently high magnification was attempted, the thinner carbon films fixed on microgrid meshes were adopted for the specimen support. The electron microscope applied for the observation was JEM-7A which was operated under 100 kV acceleration. The electron-optical magnification was 6,500x for taking the direct photomicrographs.

RESULTS AND DISCUSSION

Although the silver sols used here ranged in a wide variety as far as the preparing condition was concerned, the correlation between this condition and the particle structure will not be the major concern in this report. Instead of it, much attention has been concentrated to the characteristic configuration which is common to all samples of silver sol. As to the size distribution, it ranged from 100 A to 1000 A and the most probable size was about 500 A in general. It was rather difficult to find out precise distribution curves since no particles excepting a few were likely to assume definite shape but mostly appeared in various irregular forms which were nearly sphere or spheroid. The irregularity in shape seems to have been caused by the substructures such as twins, stacking faults and other lattice disorders which gave rise to characteristic contrasts in the final electron images.

1. Identification of Particles

The electron diffraction was applied to small areas of the specimen where comparatively large number of particles were present. The selected area diffraction thus obtained appeared as spotty Debye-Scherrer patterns one of which is displayed in Fig. 1 for the example. The analysis of these diffraction patterns indicates that the most of the rings are ascribed to silver as indicated in Fig. 1. The extra ring is considered due to systematic double reflection which is also associated with the regularities in the orientation of smaller crystallites in the individual particles as will be discussed later.



Fis. 1. Debye-Scherrer pattern obtained by electron diffraction of silver sol particles. The innermost reflection (e) is due to the double diffraction associated with the multiple twin structure. Other rings indicated by arrows are for ordinary reflections from f.c.c. silver.

2. Various Contrasts and Substructures

One of the most remarkable features of the anomalous contrasts in the electron images is the parallel striped patterns as shown in Fig. 2 with several examples. These striated contrasts are ascribed to diffraction contrasts caused by the lattice defects involved in the individual particles. Since the striations appear in parallel orientation, it seems reasonable to deduce that each particle is essentially a single crystal and the lattice defects are associated with a simple group of lattice planes. In the case of the face-centered cubic lattice (f. c. c.)

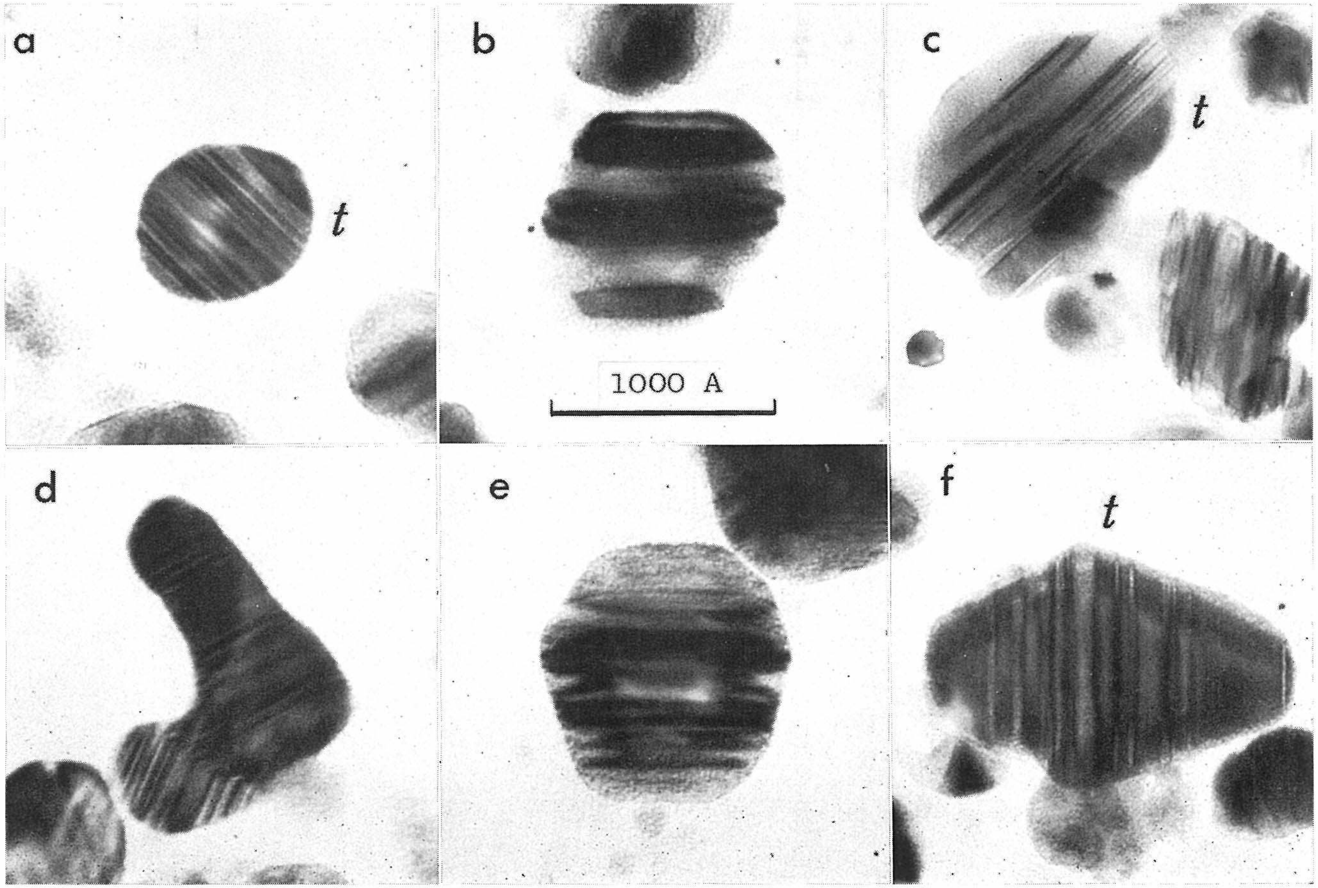


Fig. 2. Striated diffraction contrast due to stacking faults in silver sol particles. t : twin structure

which is also the one assumed by the metallic silver, it is well accepted that characteristic defects and disorder generally occur in the (111) plane which is the most densely packed plane. As to the lattice disorder which gave rise to the striated contrasts of silver sol particles is considered as the stacking faults where the cubic lattice partly assumes an hexagonal close pack layer. There are a few remarkable features in regard to the contrasts of these striations. The narrow background regions located between two of these striations generally appear with the same lower contrast than that for the striation itself. In some cases, however, the narrow band areas assume much darker contrast as designated as *t* in the photos. These differences of contrast are attributed to the different orientation of the crystal lattice contained in the area, since the variation of lattice orientation changes the condition of electron diffraction which is essentially the origin of the image contrast. The change in the lattice orientation defined by the (111) plane is interpreted in terms of the twin formation where the (111) plane is considered as the composite plane of the twin, in other words, lattice orientation of the darker band can be reproduced if the total lattice for the lower contrast area is rotated by 180° around the axis normal to the composite plane.

The other characteristic aspect of the striations is that some of them never cross over the total crystal particle but extend only part of the way in a manner of an edge dislocation. When the stacking fault plane is viewed in a direction almost parallel to itself, the contrast appears as a striation. However, it would trace a loop as the intercept of the fault plane and the crystal surface as shown in Fig. 2 b and e, when the fault plane makes rather large angle against the incident electron beam. It should be noted that these loops of higher contrast is accompanied by thinner and smaller subsidiary loops with definite intervals between them, although the origin of these effects is not fully understood at present.

3. The Crossed Stacking Faults

The stacking faults were often formed with much more complicated configurations where the fault planes appeared not only in parallel but also in variously crossed states holding a definite angle between them. Some examples of electron photomicrographs were reproduced in Fig. 3. The characteristic aspects of crossed faults are rather explicitly shown here. The parallel striations designated as X and Y are both set of parallel stacking faults, the band structure of which is essentially the same as those explained in the above section. The conspicuous difference, however, is that these parallel bands, X and Y, are crossed each other at an angle of 72° in both cases. As illustrated in Fig. 4, four {111} planes with different orientations can be defined in the f. c. c. lattice, surrounding a tetrahedron such as ABCD whose edges are composed of six diagonals of the cube facee. When such a tetrahedron is viewed along [110] direction parallel to, for instance, the diagonal CD, two kinds of {111} planes ADC and BDC appear as two crossing lines which hold an angle of 70.5° between them. Since this angle is in good accordance with those which appeared in regard to the crossing sets of parallel striations as in Fig. 3, it may be reason-

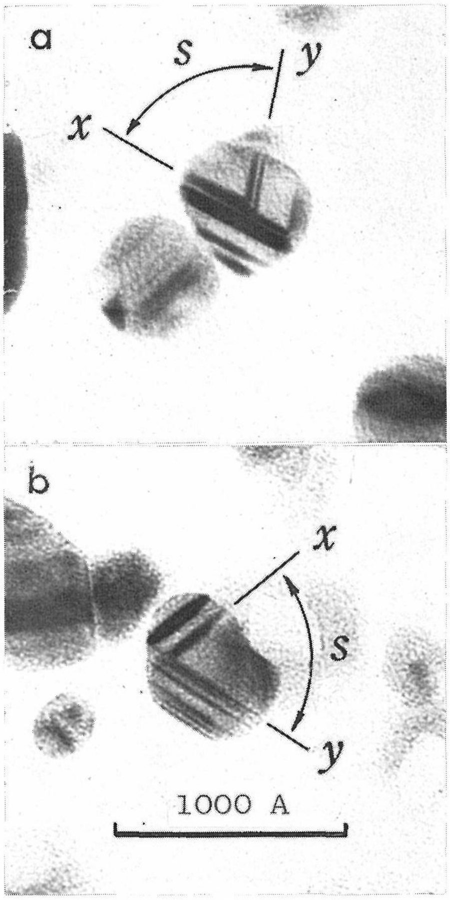


Fig. 3. Crossed stacking faults of silver sol particles.
The angle (s) between x and y is about 70°.

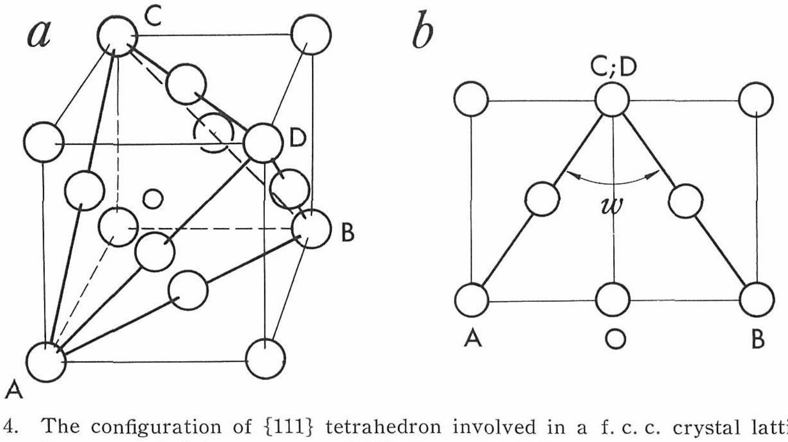


Fig. 4. The configuration of {111} tetrahedron involved in a f. c. c. crystal lattice.
The angle (w) between two (111) planes is 70.5°.

able to deduce that the stacking faults were formed in two kinds of {111} planes with different orientations in the same crystal. In this case, the particle itself is basically a single crystal, since the narrow band areas which form the background of the striations assumes the same contrast all over the individual particles. However, the configuration appears much more intricated as to the particles shown in Fig. 5 in which the twin formation is also observed. For instance, the particle in a, which is almost 800 A in diameter, has a vertical band with a lower contrast in the middle whereas the crystalline backgrounds

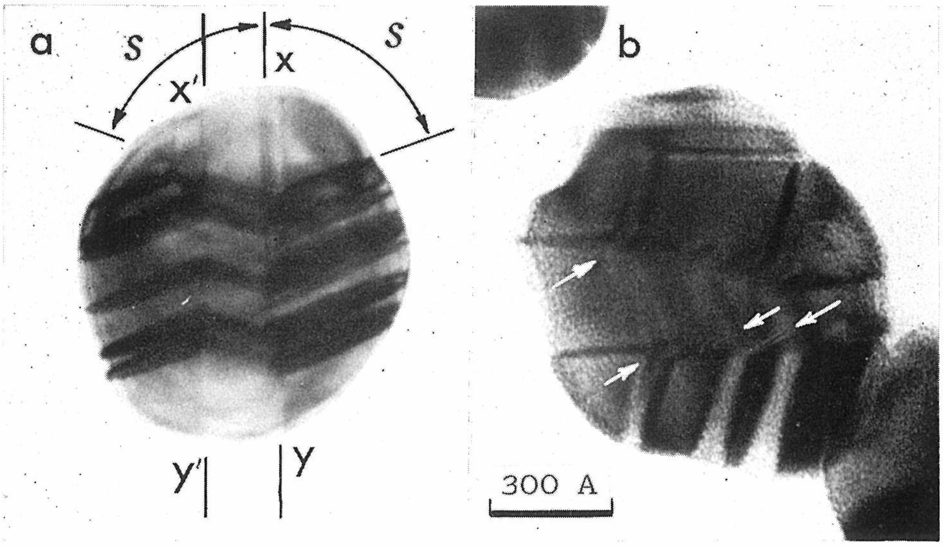


Fig. 5. The silver sol particles which contain parallel twins and stacking faults. The angle s is about 70°. White arrows show moiré patterns with 15 A spacing.

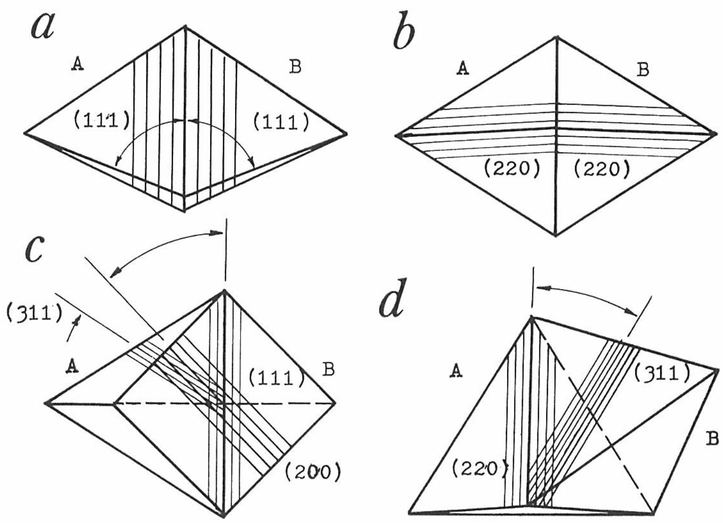


Fig. 6. Demonstration of simple twin formation and the mutual orientation of various lattice planes which contribute the diffraction contrast and double reflections.

on both sides assume the same higher contrast than the middle band. The boundary lines are considered to be (111) planes, since the striations also make angles 72° on both sides of the boundary. Such a configuration can be well illustrated with the schematic diagram in Fig. 6 a, where the orientation of twinned crystal pair is demonstrated with (111) tetrahedra which shear a common vertical (111) facet as the twinning plane. The striations and the loops due to stacking faults that are supposed to lie in other {111} planes such as ACD and A'CD appear in a manner of symmetry with the twinning planes XY and X'Y' as the mirror planes in the actual particle. It is interesting to note that some of the striations and loops are continuous all over the particle although they change orientation at the twin boundaries. Similar configurations are also observed with the particle in Fig. 5 b, although very narrow stripes with a spacing of about 15 A appeared around the intercepts of boundaries as shown by white arrows. Since there is no lattice spacing larger than 2.35 A in silver crystal which gives rise to reflection, these stripes are considered as the moiré fringes caused by the repeatedly reflected electron waves at different type of lattice planes in two successive crystallites. The fact that the direction as well as the spacing is the same to all moiré fringes indicates the regularity that exists in the mutual orientation of the crystallites in the particle.

These substructures are considered to be closely connected to the mechanism of particle formation although the detail has to be left to further careful investigation.

4. Multiple Twins

One of the most predominant configurations assumed by the dispersed particles of silver sols is the multiple twin structure which consists of five to twenty tetrahedral crystallites surrounded basically by four {111} planes. The examples are presented in Fig. 7, where particles contain triangular domains with various contrasts separated by radial boundaries rather than the parallel striations as in the examples of former cases. The appearance of domains with different contrasts clearly indicates that each particle consists of smaller crystallites which are oriented in various ways. The triangular shape defined by the boundaries seems to have a close connection to the tetrahedron formed by four {111} planes. This deduction is also evidenced by the multiple fringes which roughly trace the outer perimeter of tetrahedron projected on the viewing screen or photoplate as indicated by arrows in Fig. 7, c and d. The configuration based on regular arrangement of {111} tetrahedra was first proposed by Ino[5] with respect of small nuclei of f. c. c. metals which were deposited onto a clean cleaved face of rock salt crystal in an ultra high vacuum evaporator. According to his deduction, a total particle can be constructed by the successive addition of tetrahedron of the same size so that every two of them should shear a basal regular triangle, finally resulting in multiple twin structure. The simplest example is the case shown in Fig. 6. Although various combinations can be considered as the number of tetrahedron increases, the most possible form suitable for the present case is considered likely to assume a decahedron which consists of five tetrahedra as illustrated in Fig. 8. Such an arrangement of the elementary crystallites well explains the appearance of radially asteriated boundaries which define the domains with various contrasts. In some cases, one or two boundaries disappear leaving

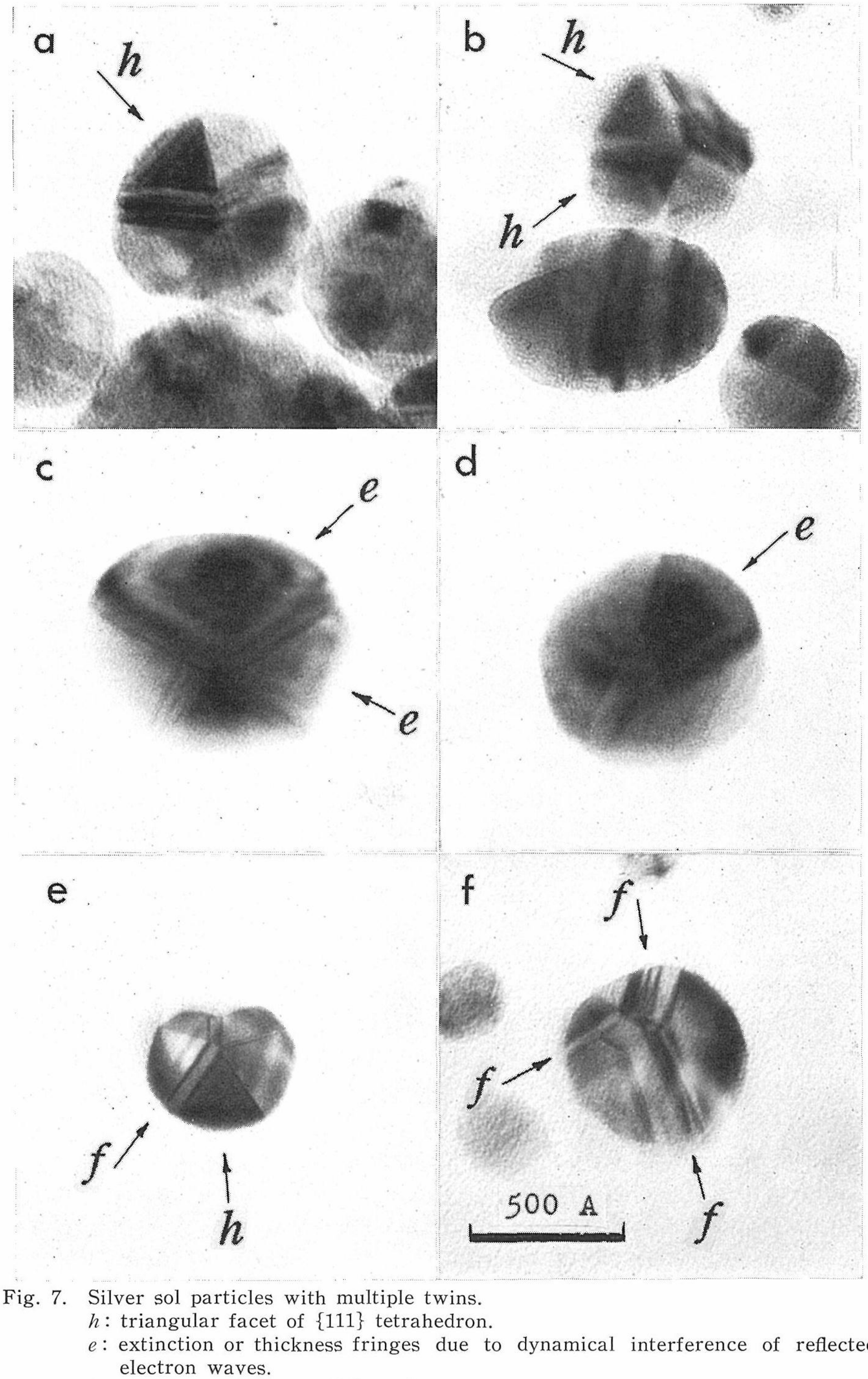


Fig. 7. Silver sol particles with multiple twins.
h: triangular facet of {111} tetrahedron.
e: extinction or thickness fringes due to dynamical interference of reflected electron waves.
f: stacking fault in multiple twins.

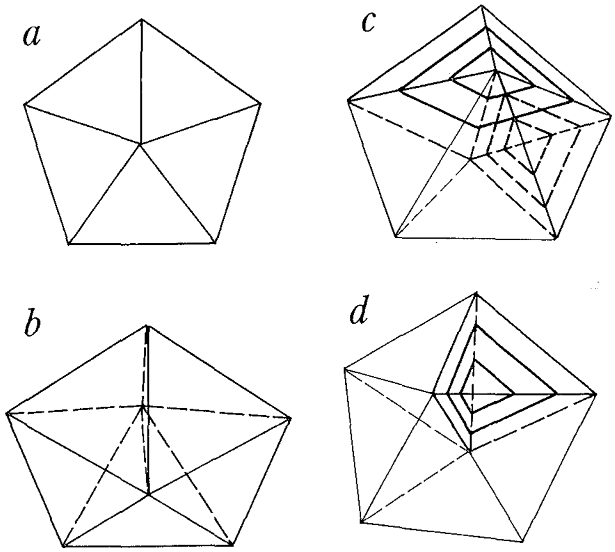


Fig. 8. Perspectives of decahedron and the formation of thickness fringes which discriminate the orientation of {111} tetrahedron.

rather wide rhombic area with the same contrast. This effect is caused by the diffraction condition due to the orientation of a pair of twinned crystallites. As shown in Fig. 6, b, there exist {220} planes, for instance, which are normal to the basal plane and common to both twins. When the contrast is governed by the reflections from these common planes, the result is the disappearance of the boundary line.

The perspective of the pentagonal decahedron in Fig. 8 is also useful to explain how the multiple fringes in Fig. 7 c and d follow the perimeter of the crystallite in a particle as illustrated in Fig. 8. c and d. These fringes are known to be caused by the interference of electron waves repeatedly reflected by the same lattice plane and usually called the thickness fringes or extinction fringes, although the detail will not be discussed here.

As the multiple twin structure also defines the mutual orientation of these elementary tetrahedra, it very often takes place that the electron beam that is reflected by a particular plane happens to be reflected back to a certain position by other lattice plane of other tetrahedron causing an extra spot in the final diffraction pattern. In this case, the combination of pair of lattice planes must require a certain orientation of the pair to the incident electron beam for such double reflection to occur. Some possible sets of double reflecting planes were detected by a systematic analysis as displayed in Fig. 6 c and d, which gave rise to the extra ring in the diffraction pattern presented in Fig, 1 when the electron beam was incident normal to the plane of figures. This is the reason why the appearance of such extra reflection also evidences the regular arrangement of elementary crystallites in the individual sol particles.

Another important feature for the multiple twins in the case of colloidal particle is that the elementary tetrahedron itself very often contains stacking faults which have never been reported to be observed in other particles[5,6] prepared in dry system, though such a complicated substructure was also detected in the case of collidal gold such as Faraday sol, Weimarn sol and sodium citrate sol as will be reported elsewhere. Fig. 7, e and f are the examples of such combined configurations of multiple twins and stacking faults.

When the mechanism of the nucleation of these sol particles is studied, it seems advisable to take such a different behavior into account. It also seems worthwhile to notice that the multiple twin structure stands not only for the nucleation of metallic particles in dry system such as vacuum condensation or sublimation in an atmosphere of inert gas but also for the nucleation from solutions. This phenomenon is likely to be a rather common effect and may be found also in the case of nucleation caused by a solid reaction.

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